PRACTICAL TANNING WITH GLUTARALDEHYDE

Wallace Windus

Summary

The tanning action of glutaraldehyde has been studied in detail at our laboratory by Dr. E. M. Filachione and his associates. Demonstration of its applicability and the availability of this chemical at an economically feasible price has led to its commercial use by the leather industry in the United States. This paper will summarise our information about the reactivity, methods of use and commercial applications of this aldehyde, together with the properties of the leather.

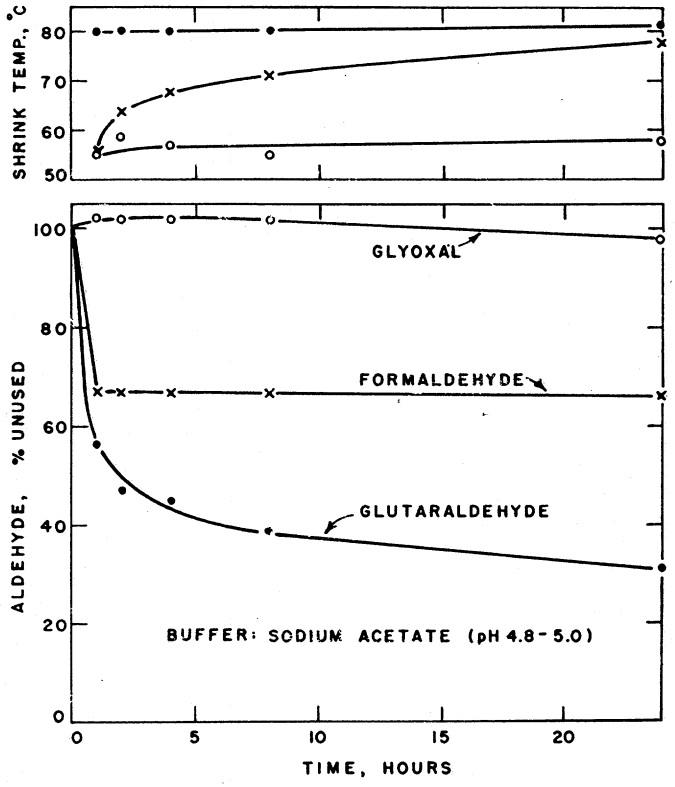

FIGURE 1
Comparison of rates of tanning at pH 5 (approximately).

Comparison with other Aldehydes

Figure 1 shows the reactivity of glutaraldehyde in comparison with glyoxal and formaldehyde buffered at a pH of about 5 to have a uniform pH for research purposes. Twelve per cent of a 25% commercial aqueous solution of glutaraldehyde was used and amounts of formaldehyde and glyoxal equivalent to this; namely 4·9% formaldehyde and 5·8% glyoxal. The

per cent glutaraldehyde used will be expressed as the amount of the 25% solution throughout the rest of the paper. Single Syrian sheepskins were used in this experiment.

The graph indicates that 60% of the glutaraldehyde has reacted with the skin in 6 hours whereas only 32% of the formaldehyde has reacted. Glutaraldehyde is, therefore, roughly twice as reactive as formaldehyde at a pH of 5. The shrink temperature of glutaraldehyde-tanned leather attains its maximum rapidly whereas that of formaldehyde rises gradually. Glyoxal has essentially no tanning action at this pH.

Figure 2 shows the results obtained by the same procedure except that the skins were buffered at a pH of approximately 8. More than 90% of the glutaraldehyde has reacted with the skin in 5 hours, whereas only 40% of the formaldehyde has reacted. Furthermore, there is little additional

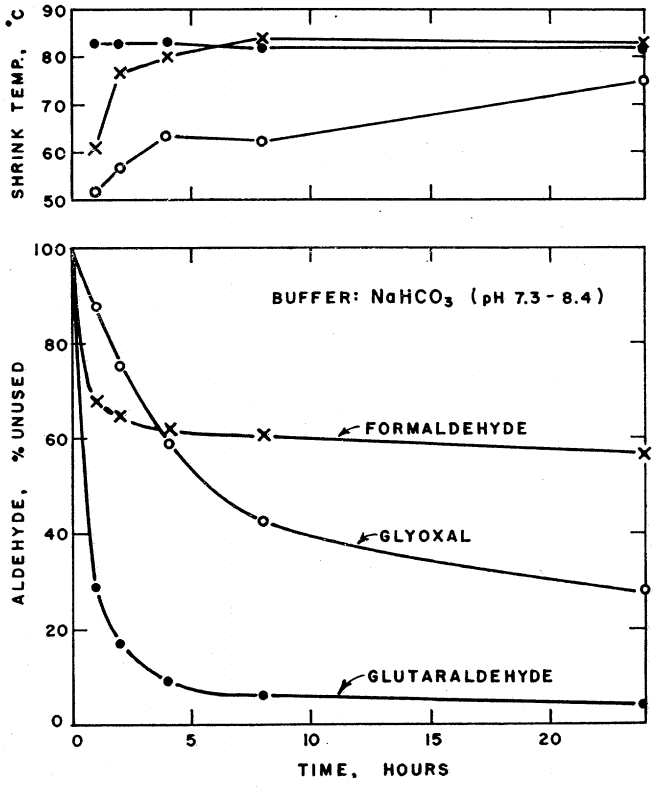

FIGURE 2

Comparison of rates of tanning at pH 8 (approximately).

reaction of formaldehyde with an increase in time. Glyoxal is fixed in significant amounts in this pH range and continues to react during the 24-hour period. However, only 45% has reacted in 5 hours and 72% in 24 hours.

Procedures

Tanning with Glutaraldehyde Only

Figure 3 shows the rate of tanning with glutaraldehyde at different pH values. As with other aldehydes, the rate increases with increasing pH. While there is some reaction at pH of 2 the graph shows that it is safe to add all of the aldehyde to pickled skins and raise the pH gradually for uniform penetration and smooth, well let-out leather.

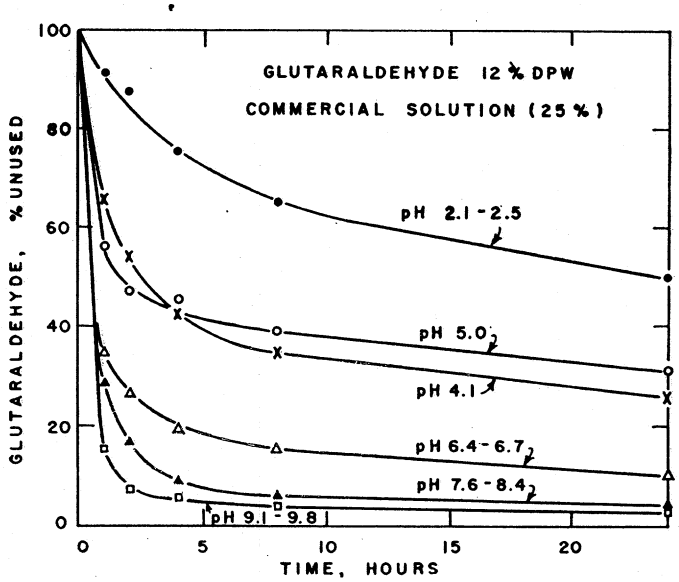

FIGURE 3

Rate of tanning with glutaraldehyde at various pH levels.

Accordingly, the following is a practical procedure when tanning with glutaraldehyde alone and is in commercial production.

Pickled skins	100%
Water	100%
Sodium chloride	6%
Glutaraldehyde (25% solution)	12%
Drum ½ hr. pH 2·3	
Sodium formate	4%
Drum 1-2 hr. 4·0	
Sodium bicarbonate	3%
Drum 1 hr. pH 6·6	

Sodium bicarbonate	0·5%
Drum 2 hr. pH 7	
Formic acid ...	1·75%
Drum ½ hr. pH 4·4	
Wash ½ hr. Shrink test 83°C.	

The procedure is straightforward and is designed to be completed during an 8-hour working day. While the skins can be left in the drum overnight, there is danger of streaks of colour if glutaraldehyde is present in the liquor when the drum is stopped.

Sodium sulphate can be substituted for sodium chloride. Sodium sulphate is preferable if the pH is to be raised above 7 since the sulphate is known to be more effective in repressing swelling than the chloride. The glutaraldehyde can be added in feeds approximately ½ hr. apart, if desired, although this is not necessary. The pH values and times can be modified within reasonable limits. The skins can be washed after tanning and before acidification to adjust the pH for fatliquoring. If this is done, greater care must then be exercised to avoid too low a pH upon acidification. Direct acidification of the tan liquor provides an automatic buffer control due to the presence of sodium formate, although the rapid liberation of carbon dioxide may be objectionable.

This procedure specifies 12% of the commercial glutaraldehyde solution (3% of 100% glutaraldehyde) on the drained pickled weight. This is a full tannage. Ten per cent is adequate on sheepskins for many purposes. Sheepskins usually contain more water than other skins or hides in the drained pickled condition. Therefore, it may be desirable to use as much as 15% glutaraldehyde on side leather when glutaraldehyde is the only tanning agent.

Simultaneous Tanning with Glutaraldehyde and Basic Chromium Sulphate

Figure 4 shows the result of adding glutaraldehyde to a chrome liquor. The system was buffered to have a constant pH of 3·6 to 3·8 for research purposes. These data were secured by tanning pickled Cabretta sheepskins.

The broken lines are the single tannages, either glutaraldehyde alone or chrome alone. The solid lines show the rate of uptake of glutaraldehyde and of chrome when a mixture of 6% glutaraldehyde and 4% Tanolin R*, a 33% basic chromium sulphate containing the equivalent of 24% Cr_2O_3, is used. Since all lines are essentially identical, there is obviously no interference with the tanning action of either compound by the other. In this instance, in which half the usual amount of chrome was used, the shrink test of the combination glutaraldehyde-chrome tannage is somewhat higher than that obtained with 4% of chrome alone.

Keeping in mind the slower tanning action of glutaraldehyde at the pH used for chrome tanning it is advisable to use less glutaraldehyde than would

* Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

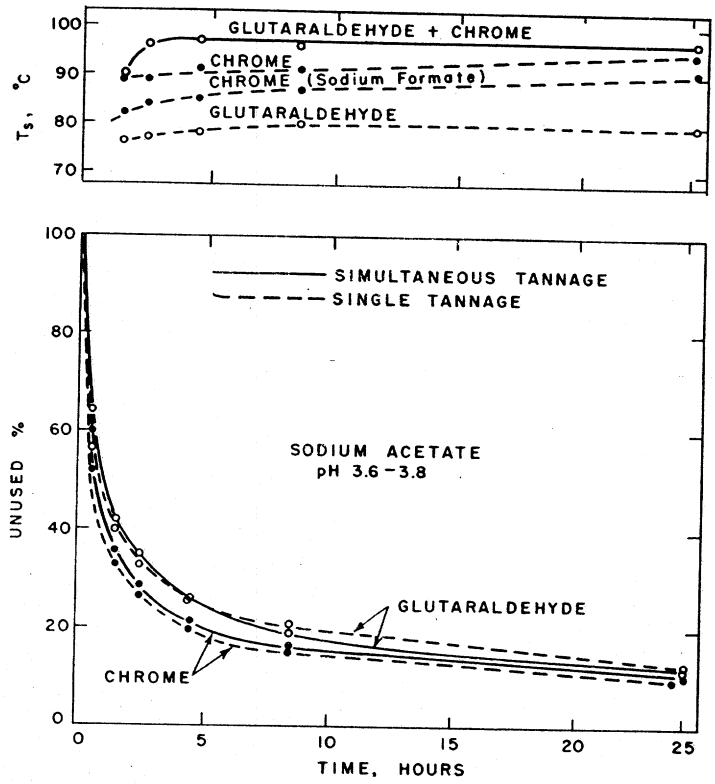

FIGURE 4
Simultaneous tanning with glutaraldehyde (6% d.p.w.) and chrome (4% d.p.w.) at pH 3·6–3·8.

be used in the single tannage. This will give a greater percentage utilisation and reduce the danger of streaks if the skins are left in the drum overnight. It is also advisable from the standpoint of economy since less glutaraldehyde is needed for a complete tannage when used with chrome. It would seem reasonable, however, to use not less than 4% of the commercial aqueous solution of glutaraldehyde. This will provide 1% of actual glutaraldehyde on the pickle weight and is about the minimum amount that will modify the properties of the leather significantly.

Figures 5 and 6 show the rate of uptake by a pickled grain split of a cattle side when tanned with 6% each of glutaraldehyde and chrome in the same tanning liquor. The rate of tanning and total uptake are greater at a pH of 3·7 to 4·0 than at 3·1 to 3·4, as would be expected. The pH is more important than the kind of neutralising agent used, although formate no doubt retards the rate of chrome tanning due to the formation of the chromium formate complex.

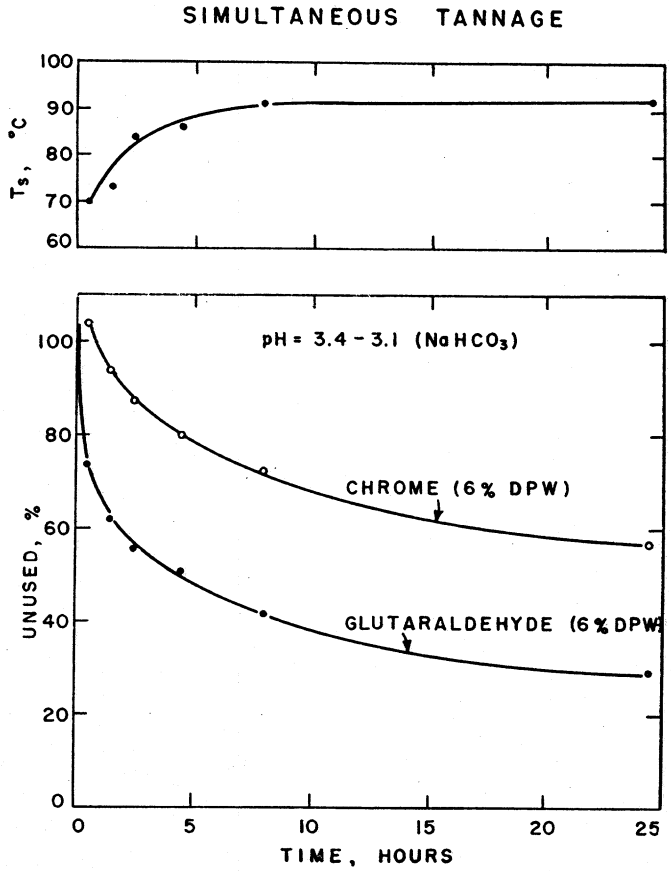

FIGURE 5

Simultaneous tanning with glutaraldehyde (6% d.p.w.) and chrome (6% d.p.w.) at a pH of 3·3 (approximately).

This is a convenient way to use glutaraldehyde since it is added to the regular chrome tannage with no change in the procedure.

Retanning Chrome-Tanned Leather with Glutaraldehyde:

Figures 7 and 8 show the retannage of single sides of chrome-tanned grain split cattlehides with 6% and 10% of glutaraldehyde based on the blue shaved weight. These were run at room temperature. Again the rate of tanning is faster at pH 4·3 than at 3·4. Note that the shrink temperature is essentially unchanged by the glutaraldehyde when the leather has had a full chrome tannage.

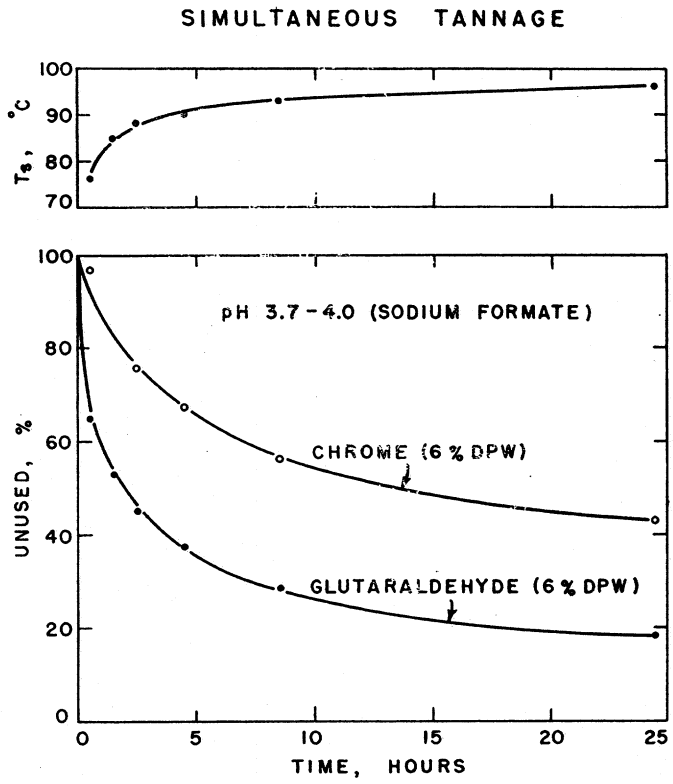

FIGURE 6

Simultaneous tanning with glutaraldehyde (6% d.p.w.) and chrome (6% d.p.w.) at a pH of 3·8 (approximately).

Figure 9 shows the effect of an elevated temperature on the rate of retanning with glutaraldehyde. This was run on one side in a small drum and the temperature dropped from 63°C to 47°C (145°F to 116°F) in 3 hours. The rate was rapid in spite of a pH of 2·9 to 3·6.

Retanning chrome-tanned leather with glutaraldehyde at an elevated temperature is a procedure that we recommend. Many American tanners like to have one chrome tannage for their whole production. After wringing, splitting and shaving, the leather is sorted and retanned by different methods for specific end-uses. Glutaraldehyde can be one of these retannages. On a large pack one has the advantage of a relatively uniform temperature and greater mechanical action. The retanning is thus completed in 1 to 2 hours, using 5 to 10% of glutaraldehyde at 49°-60°C.

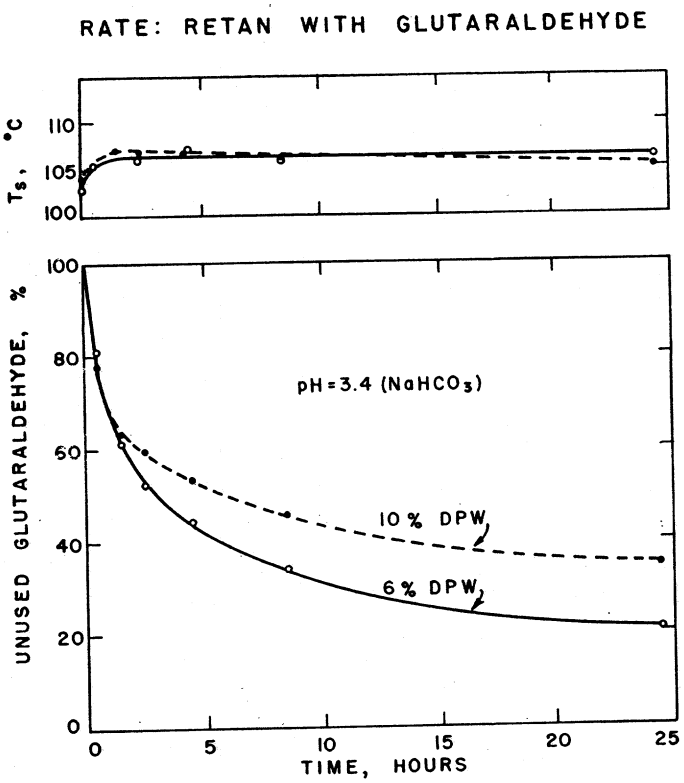

FIGURE 7
Retanning with glutaraldehyde at room temperature and a pH of 3·4.

Properties of the Leather

The maximum hydrothermal stability (shrink test) of leather tanned with glutaraldehyde alone is 85°C. This is a disappointment to us. A shrink test above 90°C would provide complete protection in all regular tannery operations, including paste drying in heated tunnels. It would also meet most United States military specifications, some of which require a minimum shrink test of 90°C. An additional mineral tannage, in moderate amount, is necessary to obtain a shrink test above 90°C.

Glutaraldehyde-tanned leather is easy to fatliquor. Fatliquors used on the regular production have given good results. This in itself indicates that the tannage is different from a formaldehyde tannage which is usually considered to be somewhat difficult to fatliquor. The tannage can be thought of as an organic tannage. The properties, therefore, resemble those of vegetable-tanned leather more closely than they resemble the properties of an inorganic tannage such as chrome. More fatliquor can be used on glutaraldehyde leather than on chrome leather. In fact, more oil is sometimes

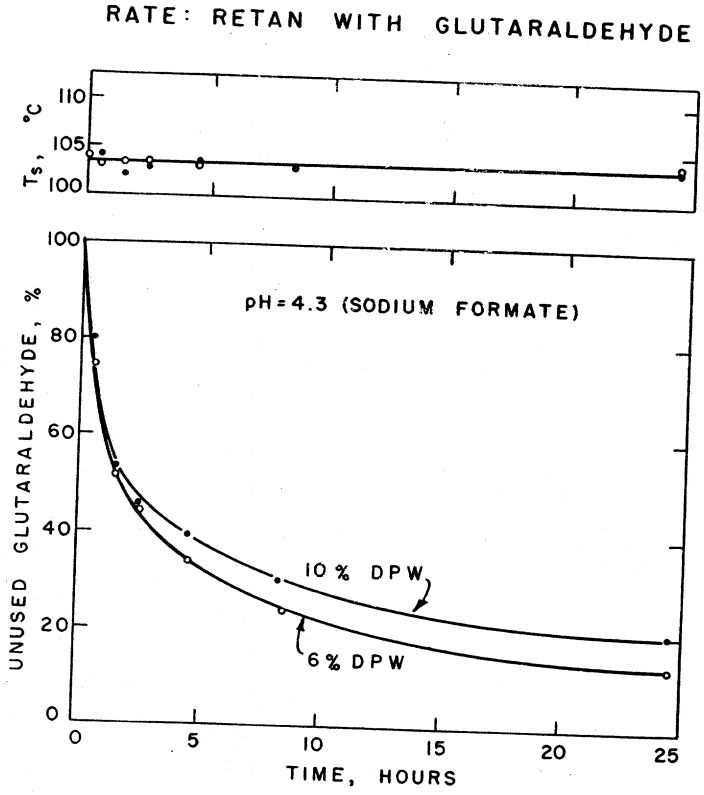

FIGURE 8
Retanning with glutaraldehyde at room temperature and a pH of 4·3.

indicated to avoid a dry feel. We have made no special study of fatliquors since there has been no necessity to do so.

The colouring or dyeing of the leather has been normal using regular dye formulas. The only complication is that the shade is changed because of a different base colour. This is true of any modification of a tannage. The off-white or creamy colour of straight glutaraldehyde-tanned leather changes to a pastel blue shade in the direction of green. This can cause a problem when a light shade is desired. However, reds are intensified so that less dye is needed. When chrome is present there is less change since the base is still bluish. One tanner who retans chrome leather with glutaraldehyde reports that his leather is clearer and brighter.

As indicated, the colour of leather tanned with glutaraldehyde is light yellow. This is undesirable for white leather, particularly since customers are accustomed to a blue-white rather than an ivory white. Nevertheless, where titanium dioxide and China clay are drummed into the leather at the end of fatliquoring and pigment finishes are used, white leather can be made.

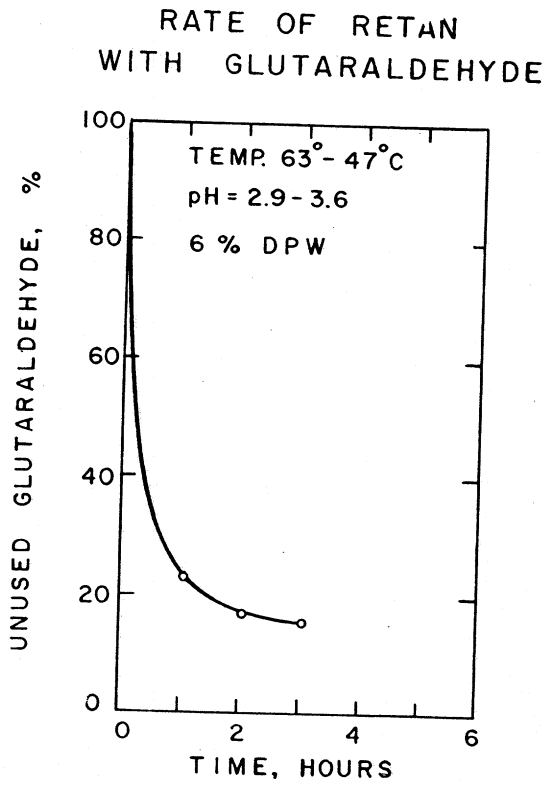

FIGURE 9

Retanning with glutaraldehyde at an elevated temperature.

The light restistance of the leather is not a problem. In a Fadeometer the colour bleaches to a lighter shade.

Leather tanned with glutaraldehyde alone is much more water absorbent than chrome leather. The leather resembles vegetable-tanned leather in this respect. This is a disadvantage in shoe and garment leather. If chrome is present the wettability is reduced substantially. When glutaraldehyde is used as a retannage on the regular chrome-tanned leather, the wettability is not altered appreciably from that of the regular leather.

This aldehyde used alone yields a mellow leather. It also increases the mellowness of a combination tanned leather in proportion to the amount used. This property led to the first commercial application of glutaraldehyde to soften the backbone and neck areas of some imported sheepskins for garment leather. The rest of the skin did not become stretchy or mushy. The leather was upgraded and the cutting value improved. Unfortunately, when this aldehyde is used alone on cattle sides the leather is so mellow that the "break" is poor, and the grain wrinkles readily. Such leather could not

be used for dress shoes. As a retannage the break is not improved, but the change from the regular leather is not great.

Aldehydes are the only tanning agents in commercial use that tan on the alkaline side. This gives aldehyde-tanned leather stability to mild alkalies such as soap and sodium carbonate. Glutaraldehyde is no exception. The leather can be washed many times without becoming stiff. The shrink test is lowered only a few degrees. This has proved valuable for work shoe upper leather when the shoes are to be worn in dairies, filling stations and the like. Cleaning in such establishments is done with water solutions of relatively strong alkalies which when splashed on the shoes cause a rather rapid deterioration of chrome-tanned upper leather. Glutaraldehyde-tanned leather is more resistant and lasts much longer.

An outstanding property of glutaraldehyde-tanned leather is its excellent perspiration resistance. This property has led to new applications. Chrome-tanned shoe upper leather is being retanned with glutaraldehyde for such uses as casual shoes, skating shoes, boots and the like. It is understood that a reasonable amount of glutaraldehyde must be used to obtain this property to the desired extent. Six per cent glutaraldehyde as a single tanning agent on sheepskins is on the borderline. Twelve per cent gives high resistance. A relatively high chrome tannage (by American standards) on sides gives quite resistant leather, but even this is improved by retanning with 5% of glutaraldehyde, and 10% confers high resistance.

We wish to express our thanks to the American leather industry for their co-operation in the development of this process. Evaluation of the leather by many tanners has been most helpful. Without this assistance practical results and commercial success would have been delayed.

I also wish to thank E. M. Filachione, M. L. Fein, E. H. Harris, A. H. Korn, F. P. Luvisi, J. Naghski, and the Journal of the American Leather Chemists Association for the permission to reproduce the figures and data presented in this review.

Eastern Utilization Research and Development Division,
Agricultural Research Service,
U.S. Department of Agriculture,
Eastern Regional Research Laboratory,
Philadelphia, Pennsylvania.